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A NOVEL "GEOMETRICAL" APPROACH TO REACTION RATE DETERMINATIONS IN DETONATION

by

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A Novel "Geometrical" Approach to Reaction Rate Determinations in Detonation

Melvin A. Cook

Technical Report No. 4

Institute for the Study of Rate Processes

University of Utah

Salt Lake City

[redacted]

A NOVEL "GEOMETRICAL" APPROACH TO REACTION RATE DETERMINATIONS IN DETONATION

Melvin A. Cook

Introduction

In an attempt to provide a unification of the various experimental facts concerning the "end effect" in detonation, an empirical model of the detonation process was set up by the author, working at Eastern Laboratory, E. I. DuPont de Nemours and Co., early in World War II. (1) In spite of its entirely empirical basis, this model proved so successful that it was investigated considerably during and following the war, not only in evaluating end effects, but also in estimating reaction rates in non-ideal detonations (velocity less than hydrodynamic). In spite of the fact that the latter application of the model was "top heavy" since it involved several successive postulates, none of which had a really sound theoretical basis, it, too, proved singularly successful not only in correlating experimental observations in non-ideal detonations, but in providing absolute reaction rate data in these fast reactions which were verified in some notable examples by various direct and indirect methods.

In the investigations to be carried out under the present project, it is planned to investigate, along with various other problems, this model, both from the viewpoint of studying its fundamental basis and its application in military explosives problems. The object of this report is to describe this model in sufficient detail that it may be applied here or elsewhere in the various problems for which it is applicable, one of the most important of which is in shaped charge studies.

Model of Ideal "Detonation Head"

Consider a one dimensional detonation in a charge of constant density and composition provided with perfect lateral confinement, both as to gaseous products and heat. The explosive will be considered to fill an infinitely long cylindrical tube, with the central

axis along the x - axis , only from $x_b^o=0$ to x_a^o. The charge will be initiated at the x_b^o plane, and at instant t' the wave front will be at the x_a' plane, $(x_a' < x_a^o)$. Three possible particle velocity (W(x)) curves for the instant t' are illustrated in Fig. 1. Curve (1) is the W(x) curve for the idealized 'detonation head' postulated by the author to account for a number of experimental observations relating to "end effect" such as "cavity effect", the characteristics of sympathetic detonation, and lead block depression. The W(x) curves for $x < x_{w=o}$ are, of course, somewhat arbitrary. Curve (2) is probably a more realistic W(x) representation; it will be discussed more fully in a later report. Curve (3) at least for $x > x_{x=o}$ is the type of W(x) curve suggested by the von Neumann theory of detonation.(2) The $x_{w=o}$ plane is the 'stagnation' plane where W=0. W_{cj} is the particle velocity at x_{cj} or "Chapman-Jouguet" plane which, in an ideal explosive (one which propagates at the hydrodynamic velocity D*), corresponds to the end of the reaction zone.

The "detonation head" in this case is defined as the region between x_a' and $x_{w=o}$. The problem in determing its size is, therefore, to define $x_{w=o}(t)$. The transition from deflagration to detonation is associated not only with the formation of a "detonation wave" but also a "retonation wave". The latter is, itself, a type of shock wave which moves in the opposite direction to detonation. Each element of explosive upon reaction, even though the reaction may take place wholly in the detonation head, reinforces each of these oppositely propogating waves such as to conserve linear momentum between them. The nature of this momentum conservation is postulated in the model described here as follows: Decomposition in the "reaction zone" is assumed to give rise through momentum transfer to the boundaries of the detonation head, to an equal mass of products moving in opposite directions initially at equal velocities. In other words, it is assumed that under perfect confinement, each reacting particle of mass m contributes a mass m/2 of detonation products both to the detonation head and retonation head. The influence of pressure in

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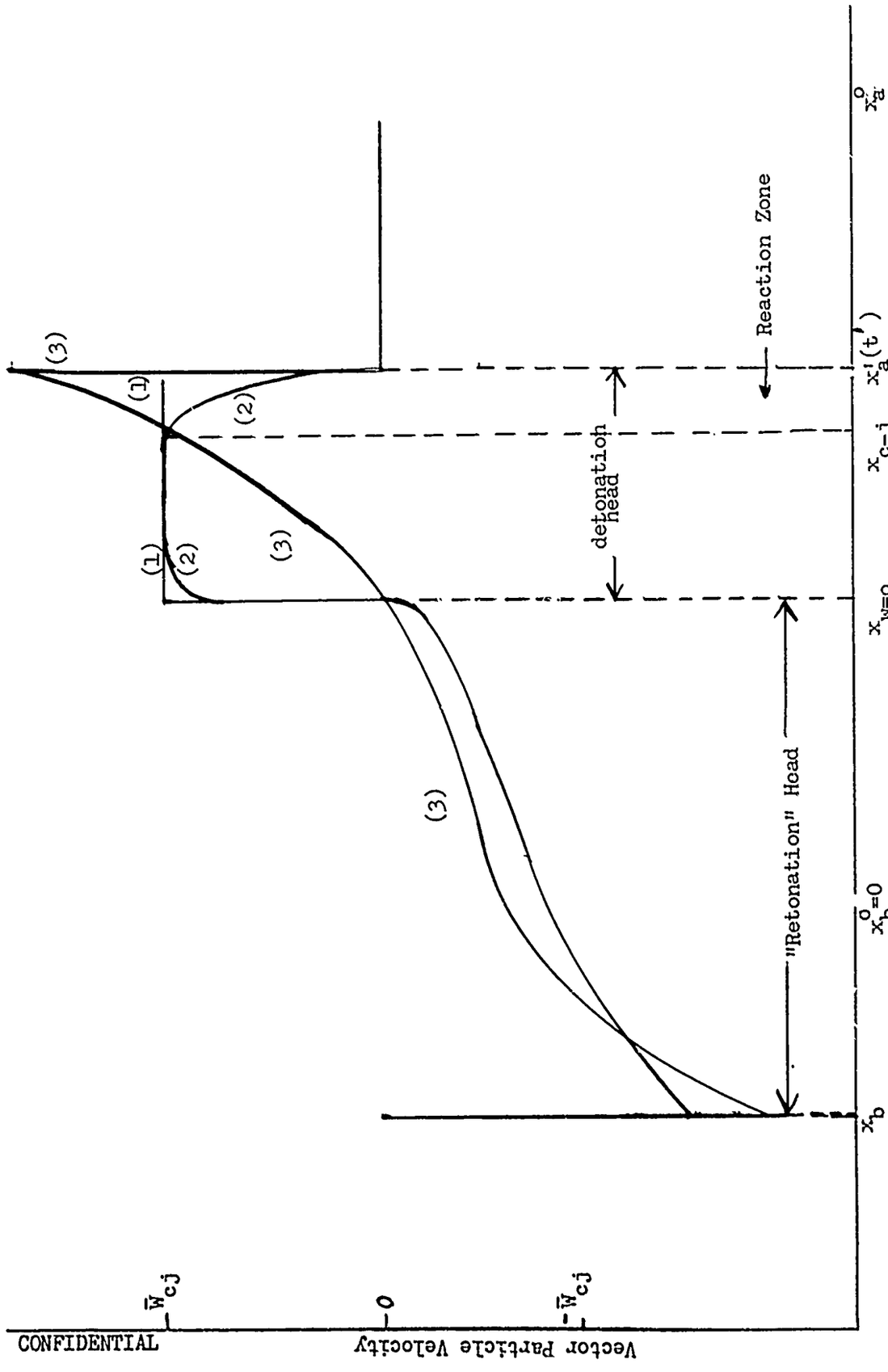


Fig. 1 Particle Velocity--Distance Representations

the detonation head and retonation head subsequently gives rise to a distribution of particle velocities W(x) characteristic of the conditions existing within the head itself. However, these pressure characteristics presumbly are not transmitted across the $x_{w=o}$ plane as far as particle velocity distribution is concerned, and, therefore, each head apparently retains its identity and characteristics throughout the detonation process. The pressure in the detonation head makes it possible, however, to convey the impulse of the chemical reaction to the rear of the detonation head and across the $x_{w=o}$ plane. This process, originating in chemical reaction, has, it is believed, the influence of flattening out the detonation head. However, when all the explosive is reacted, the detonation head rapidly assumes normal shock wave characteristics.

This model and the computed compression ratio v_2/v_1 in the detonation head (v_1 and v_2 are the specific volumes of the undetonated explosive and in the products at the Chapman-Jonguet plane, respectively) allow one to compute the ratio $x_{w=o}/x'_a$. For solid and liquid explosives, with densities from about 0.7 to 1.7 g/cc, v_2/v_1 is, in general, 0.75 $\pm$ .03 according to the hydrodynamic theory, increasing from about 0.72 at low density, to about .78 at high. Assuming then that the density is practically constant in the detonation head, in accordance with curve (1), one obtains the approximate result

$$x_{w=o}(t') \cong 0.625\ x'_a\ (t'), \text{ or } R_o \cong 5/8\ D \qquad (1)$$

(since the mass in this ideal detonation head is by postulate half the total mass of the detonated explosive existing originally between x^o_b and $x'_a\ (t')$). $R_o = dx_{w=o}/dt$ and D is the detonation velocity.

The oppositely propogating shock waves have usually been considered as a single wave, the detonation head being the compressional portion and the "retonation" head the rarefaction part of the detonation wave. This concept, however, is probably incorrect; experimentally, both seem to be shock waves which are merely backed up on each other, or perhaps, simply joined by their respective rarefaction waves. At least,

this consideration will make it easier to understand various observations, such as the sharp boundaries which can be observed between these waves in flash radiographs. The pressure in the detonation head is, of course, considerably higher than in any part of the "retonation" head, but this circumstance is probably the only resemblance of the "retonation" head to a rarefraction wave. The sharp differences between the detonation and "retonation" heads really arises from the fact that the latter is moving out into the open, while the former is moving continually into and is, therefore, confined by the undetonated explosive. Even if the tube were (ideally) closed in the back end at x_b^o, the average density in the "retonation" head would be only 80% of that in the original explosive, while that in the detonation head is about a third greater than in the original explosive. In an open tube, however, the retonation front travels at velocities (increasing with time until the explosive is all consumed) perhaps from about 1/4 D to around 1/2 D or higher. The "retonation" head structure probably corresponds closely to that in a normal unsupported shock wave except that it, like the detonation shock, is being continuously reinforced until the detonation reaction is completed. The detonation head resembles a normal shock wave probably only sometime after completion of the explosive reaction, e.g. when x_a' has reached two or three charge diameters beyond the end of the charge.

The question of whether the normal detonation head for $x_a'(t) < x_a^o$ involves the von Neumann "spike" resolves itself theoretically according to arguments developed by Zeldovitch[3], into the mechanism by which chemical reaction is initiated in detonation. If it were initiated by the head itself, Zeldovitch's arguments indicate that the head would possess the "spike", i.e., the system would jump initially to the point "B" of the Hugoniot curve for zero reaction and then follow down along the tangent to the final Hugoniot curve, approaching the stable velocity point "C" from the high pressure, high density side. If, on the other hand, initiation were to occur, for example, by radiation or by some other mechanism which allows initiation ahead of the shock, the process could, according to Zeldovitch, proceed to the stable "C" point directly

along the "Todes line" from the initial conditions (p_1, v_1) i.e., from the low pressure, low density side. A discussion of this topic will be left to a future paper, in which the latter process will be developed from the viewpoint of the heterogeneous distribution of mass in solid explosives, and of the experimental evidence of "dead pressing", the decrease of sensitivity with increasing density, and conditions for developing super-hydrodynamic velocities. Here will be mentioned one experimental observation which seems to exclude the "spiked" head, or confine the "spike" to a few molecular layers, as far as solid explosives are concerned.

One of the most accurate experimental methods for studying the size and structure of the detonation head is by means of cavity jets. It was shown in early fundamental studies of shaped charges that the jet impulse and penetrating potential may be related directly to the detonation head impulse[4]. Moreover, for detonation heads of constant size it was found that a linear relationship exists between the detonation head pressure p_2 computed by the author,[5,1,4] and the jet penetrating potential. It is possible to select explosives in such a way, however, that this empirical p_2 vs. hole volume relation should not apply if the detonation head were characterized by the "spike". Suppose, for instance, that one were to select two explosives having the same detonation pressure p_2, one having sufficiently low rate of reaction that x_{c-j} would fall back almost (but not quite) to $x_{w=o}$ while the other having such a high rate that x_{c-j} would approach very closely to x_a'. Both explosives would be ideal in the sense that they would propogate at hydrodynamic velocity D*. However, if the head were characterized by the "spike", the slower explosive should develop a greater cavity effect than the faster one. On the other hand, if curve (2) (fig. 1) were to apply, the slower explosive should remain less desirable than the fast one as a shaped charge explosive. But, if curve (1) were to apply accurately, both explosives should produce the same cavity effect. Experimentally, one finds that the slower explosive is never better in producing cavity effect than a fast explosive of the same theoretical detonation pressure, but is generally not so good. However, as the charge diameter is increased, the

magnitude of the end effect of the slower explosive approaches more closely to that of the faster one, and in large enough diameters it apparently reaches approximately the theoretical value predicted by the size of the "head" and the linear p_2 vs. hole volume (constant charge size) relationship for ideal explosives. There remains a good deal of experimental work to decide whether the slower explosive is still inferior to the faster ones only when chemical reaction is incomplete in the detonation head, or whether the reason that the slower explosive comes up approximately to its rated shaped charge potential in large diameter is that its reaction zone then becomes small compared with the total detonation head size. Experimental work will be required, in other words, to distinguish between curves (1) and (2), but present evidence already seems to eliminate the "spike" in solid explosives since the D/D* ratio is always unity in large enough sizes to realize the shaped charge effect predicted by the "flat topped" detonation head.

Perhaps more important information on the structure of the detonation head at and beyond the end of the explosive charge may be obtained from studies of sympathetic detonation. By measuring the rate of propagation of detonation over air gaps, one may show that initiation of the secondary charge requires in general the hot gas wave and does not occur by the air shock wave observed in streak photography, at least in the interval between the arrival of this air shock wave, and the front of the expanding products of detonation. On the other hand, when the hot gas wave arrives, initiation of detonation of a sensitive high velocity explosive apparently occurs without a time lag. The nature of these effective initiation vs. air gap distance plots is illustrated in fig. 2. It is assumed, in view of the nature of the experiment, that this curve represents the true velocity of the front of the detonation head as it expands freely into the open, following detonation.

The initial velocity of the effective initiation 'wave' is experimentally approximately $2W_{c-j}$ which, in high density explosives, is approximately half the normal detonation velocity D. The initial air

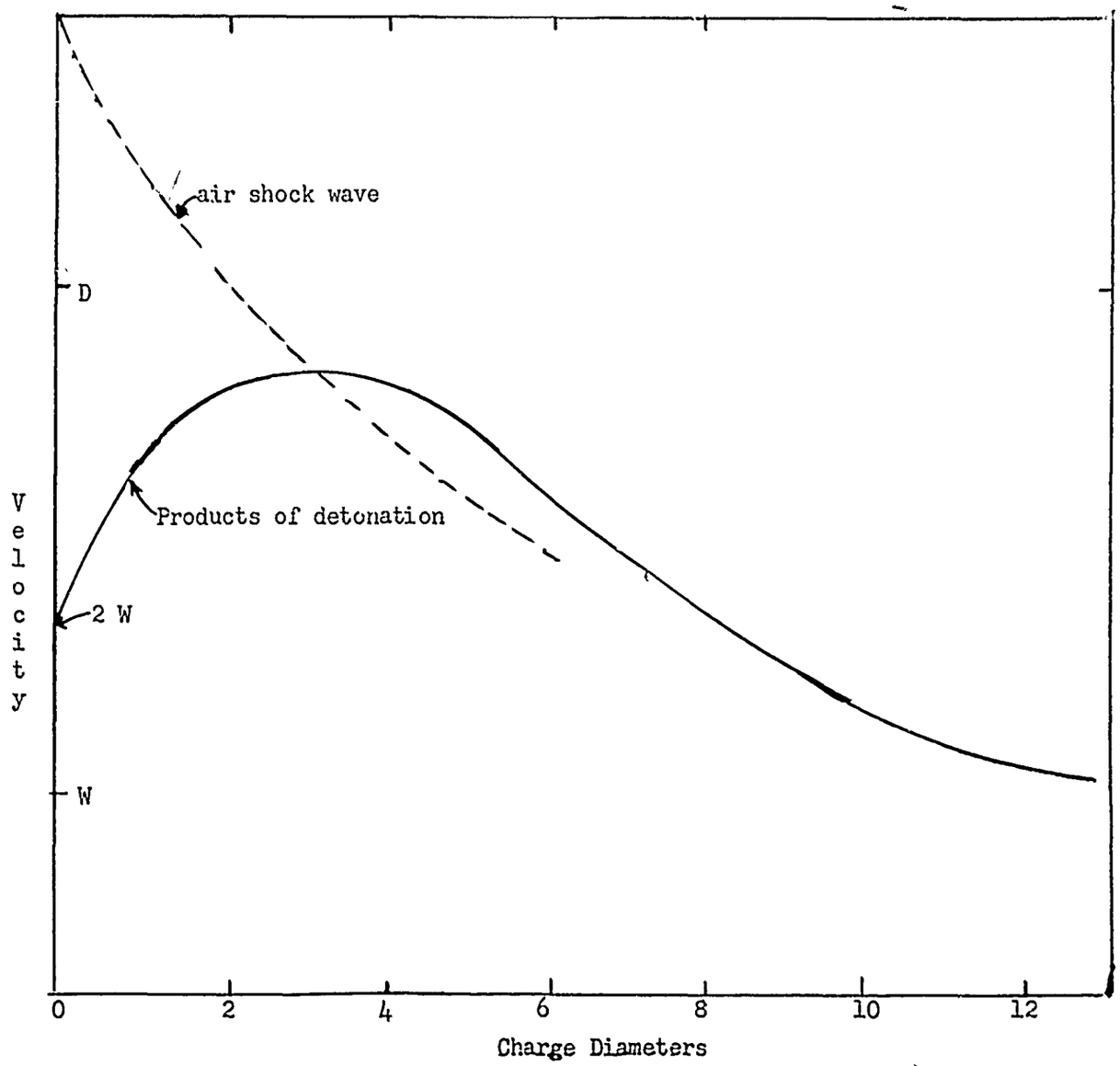


Fig. 2 Velocity of detonation head front beyond end of charge (qualitative from sympathetic detonation studies)

shock wave velocity, however, is generally considerably greater than D, sometimes approaching 2D. The effective initiation wave velocity increases rapidly over the first two or three charge diameters from the end of the charge and passes through a maximum at 3-5 diameters from the end of the charge. The air shock wave follows a far different characteristic velocity-distance curve (fig. 2). The instant the detonation wave reaches the end of the charge, a rarefaction wave should start back into the head, probably at a velocity C, the sound velocity, and the initial forward velocity of the gas in the very front of the wave should be approximately C with respect to the gas cloud which itself is moving forward at an average velocity W. The initial velocity of the expanding hot gas front might thus be expected to be D/. However, the gas in this extreme front immediately finds itself in an entirely different environment, one of lower pressure. If the pressure under which the gas in the extreme front of the wave finds itself were near atmospheric, the initial expansion velocity of the front of the expanding gas cloud, assuming it to be expanding freely, i.e., effectively into a vacuum, would be about $0.7\bar{v}$, with respect to the gas cloud velocity, i.e., approximately $W+.7\bar{v}$ with respect to a stationary point. Here $\bar{v}$ is the average thermal velocity computed from the kinetic theory, namely approximately $\bar{v}=(3RT/\bar{m})^{1/2}$ where $\bar{m}$ is an average molecular weight of the products of detonation. The initial velocity of this wave as measured in studies at Eastern Laboratory was, within experimental error, about $W+\bar{v}$ ($\bar{v}\sim 5/4\ W$), indicating that the extreme front of the wave expands, with respect to the whole wave, effectively into a medium of pressure much closer to atmospheric than to the detonation pressure. The front of the detonation head rapidly increases in velocity as $x_a'(t)$ increases beyond x_a^o, due partly perhaps to the shift from the flat topped form to a normal shock wave form similar to curve (3), fig. 1, and partly to the influence of pressure in the wave as described by the Bernoulli principle.

Edge Effects and the Detonation Head

Consider now the case of an unconfined cylindrical charge. In this case "retonation" waves will not only move backward, but also

laterally. At the front of the detonation wave, the boundary or discontinuity between the lateral "retonation" wave and the detonation head will be close to the edge or periphery of the charge, since obviously, this is its point of origin. (Experimentally, there is some evidence in shaped charge and other studies that a thin layer approximately 1/8" in thickness in an unconfined charge may not participate immediately in detonation). The (sharp) boundary between the detonation head and lateral "retonation" wave then propogates toward the center of the charge at a rate which should be the same as the velocity of the $x_{W=O}$ plane, (R_O) in the hypothetical perfectly confined charge. As a result, it eats into the detonation head until it reaches the central axis of the charge, or until it intersects the $x_{W=O}$ plane which is moving along at a velocity about 5/8 D at the back of the detonation head. Hence, the detonation head in an unconfined charge should start from the x_b^o plane, or plane of initiation, as a truncated cone with base foremost (if one could provide a plane wave initiation all across the x_b^o plane--using point initiation one would, of course, need to take account of spherical expansion of the wave front). These truncated cones grow continuously (with constant base diameter) until finally a full cone is formed, which will occur after the front of the wave has traveled 2 1/2 to 3 charge diameters from the plane of initiation. The head remains constant in shape and size during the detonation of the charge beyond 2 1/2 - 3 charge diameters. This situation is illustrated for hypothetical plane wave initiation in fig. 3. This model of the detonation head in an unconfined charge was first postulated to account for quantitative results on shaped charge effects.[4] Since then, however, this postulated conical detonation head (for cylindrical charges) has been observed in flash radiographic studies, i.e., one can observe a well defined cone of the type illustrated in fig. 3 in some of the radiographs obtained by Clark and Seeley,[6] and more recently by Dr. Jane Dewey and associates at Aberdeen.[7]

The actual velocity of the lateral "retonation" wave--detonation head boundary was determined in early shaped charge work at DuPont [4]

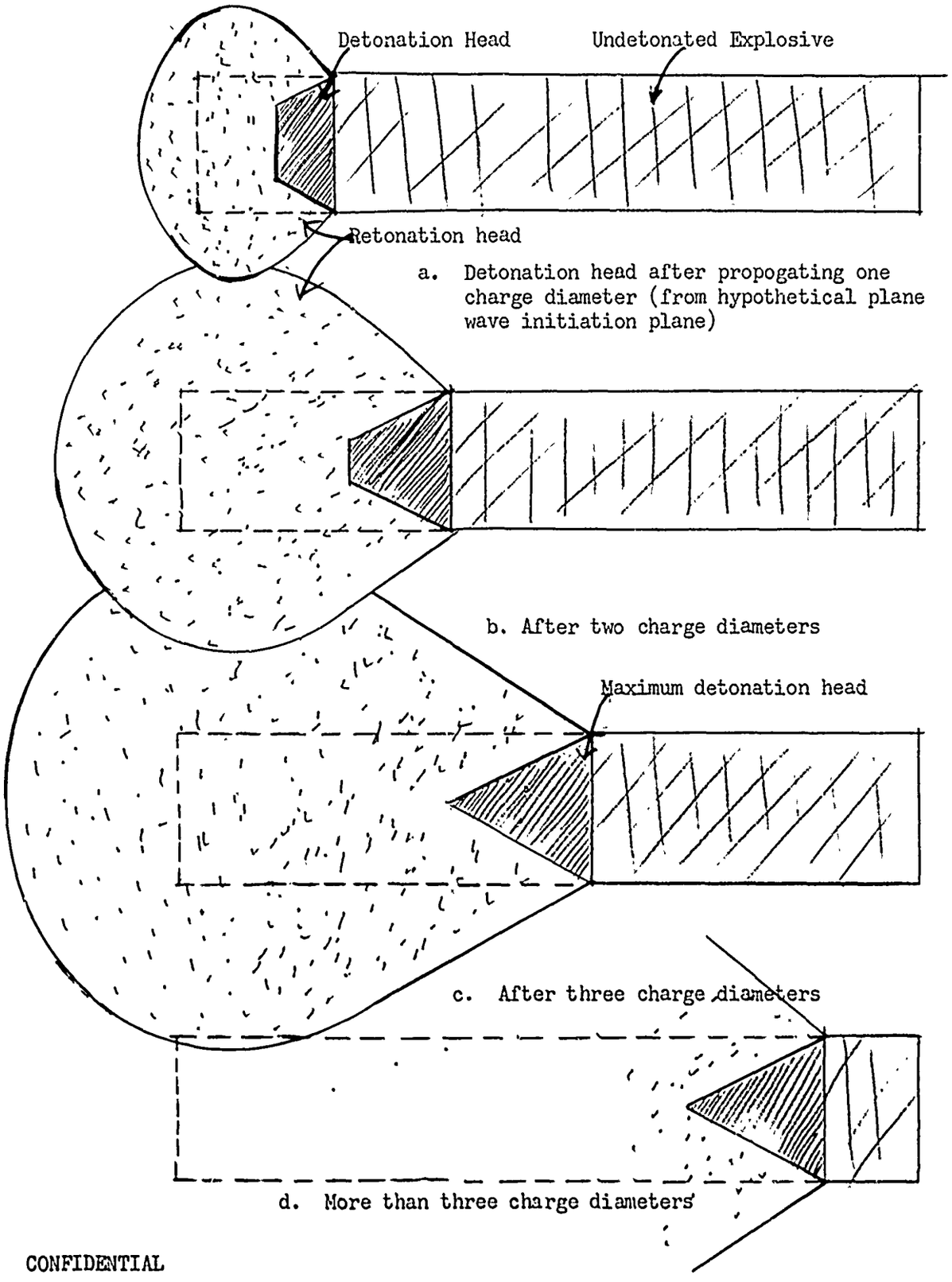
from observations of cavity effect vs. charge length in unconfined cylindrical charges of constant composition, density, and diameter. There it was found that the maximum effective charge length was 2.5 to 3.0 charge diameters, and that the cavity effect vs. charge length curve had the shape which one would predict from the above model of the detonation head, with a 'head' altitude determined by this maximum effective length. That is, if the "detonation head" in an unconfined cylindrical charge reaches its full size at 2 1/2 to 3 charge diameters, the boundary between the lateral "retonation" wave and the detonation head would have a velocity component R'_e the same, within experimental error, as that of the $x_{w=o}$ plane, that is $R_e \sim R_o$.

Incidently, the earliest model of the detonation head used by the author made use of the Langweiler postulate[8] in which the boundary $x_{w=o}$ moved at a velocity $(D+W_{c-j})/2$. Since $W \sim 1/4$ D in explosives of high density, this leads to the same result, namely $R_o \sim 5/8$ D. It is of interest that Aberdeen measurements of momentum of cavity jets carried out during World War II by Dr. Frazer gave results in excellent agreement with those computed by this model.

Detonation Head in Confined Charges

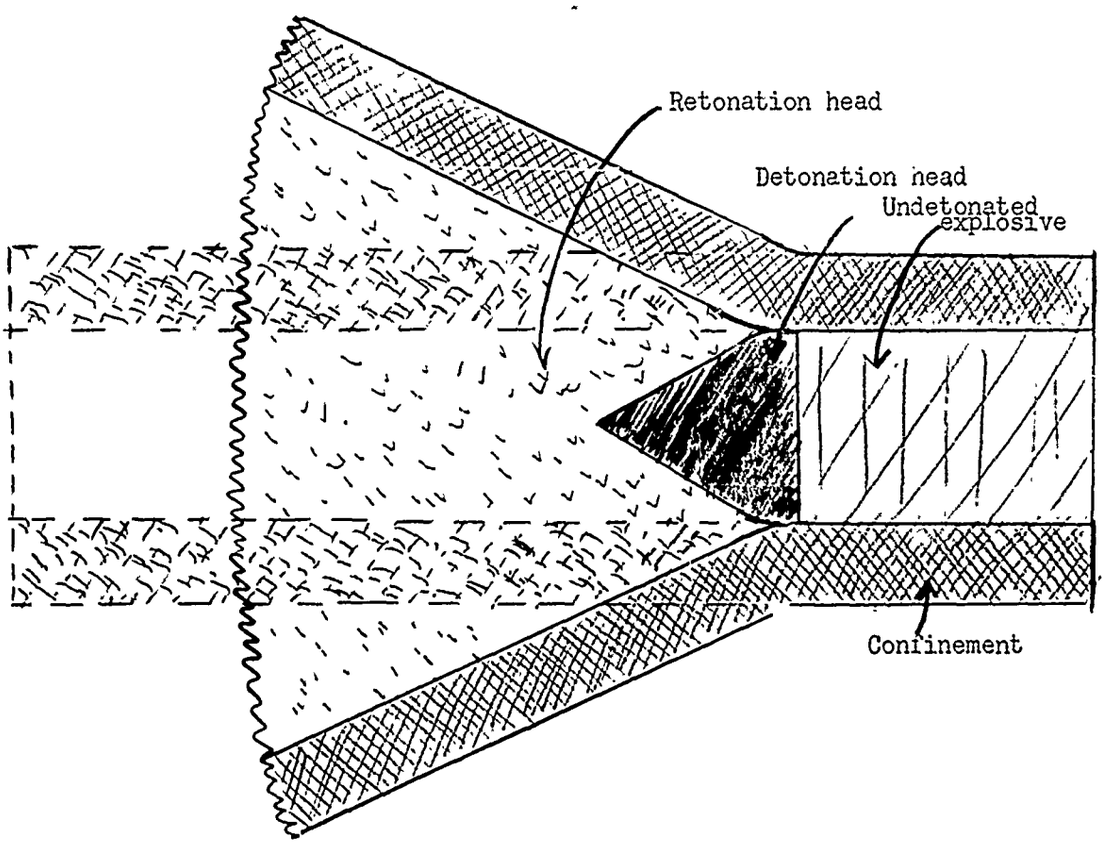
With the heaviest possible confinement for explosives of high 'brisance' or detonation pressure, the geometrical relations between the original charge and the detonation head resemble much more closely the unconfined charge discussed above than the idealized perfectly confined case treated at the beginning of this paper. The maximum effective charge length does not increase much above that for an unconfined charge. This may be shown by shaped charge studies, and by the influence of confinement on detonation velocity in non-ideal explosives ($D/D^* < 1.0$). On the other hand, the actual size of the head in a heavily confined charge is about twice that in an unconfined one of the same geometrical dimensions. This may be shown by the fact that hole volumes produced by lined cavities in heavily confined charges are about double those in unconfined charges. Evidently, therefore, the detonation head in this

Fig. 3 Development of Detonation Head in Unconfined Charge



case is not a perfect cone such as that described in fig. 3. The influence of heavy confinement is apparently to cause R_e to build up from a very low value to its limiting value over a short time interval, rather than to start out at this limiting value immediately as in unconfined charges. This situation is illustrated in fig. 4.

Fig. 4 Full Detonation Head under Heavy Confinement



D/D* and the Detonation Head in Non-Ideal Explosives

The above concept of the detonation head has been used with considerable success at the Eastern Laboratory to study the rate of chemical reaction in the detonation head in a number of commercial high explosives. Moreover, it has been possible to obtain direct checks on the total reaction times obtained from D/D* ratios with those obtained in some cases by extrapolation from low temperature thermal decomposition data, and in others by direct "rates of pressure development". It will be one of the primary objectives of this project to extend these developments to various military explosives and correlate the results with the Eyring curved front theory and with direct measurements of reaction rates. Instead of the geometry of the curved front, this method makes use of the geometry of the detonation head. For unconfined charges, the size of the detonation head should be practically independent of the density of the explosive, and the extent of the chemical reaction in the detonation head; it depends only on the charge diameter (and also charge length when the wave front is less than three diameters distance from the point or plane of initiation). The velocity of detonation will be determined by the conditions which exist along a thin cylinder within the explosive along the central longitudinal axis of the charge. If the explosive in this cylinder undergoes complete reaction within the detonation head, it will be ideal, i.e., its D/D* ratio will be unity.

Fig. 5 illustrates qualitatively the relationship between reaction zone length and the shape of the front according to the detonation head scheme for several types of unconfined ideal detonations. Some explosives which are ideal after the detonation has traveled more than three charge diameters, may not be ideal in the interval between initiation and the formation of the maximum detonation head.

If the total reaction zone in the thin cylinder along the axis goes beyond the apex of the detonation head cone, the detonation will be non-ideal not only in the region where the cone is still truncated, but also in the full coned charge beyond three charge diameters. (fig. 6)

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Fig. 5 Detonation Head -Reaction Zone Relations in Ideal Detonation

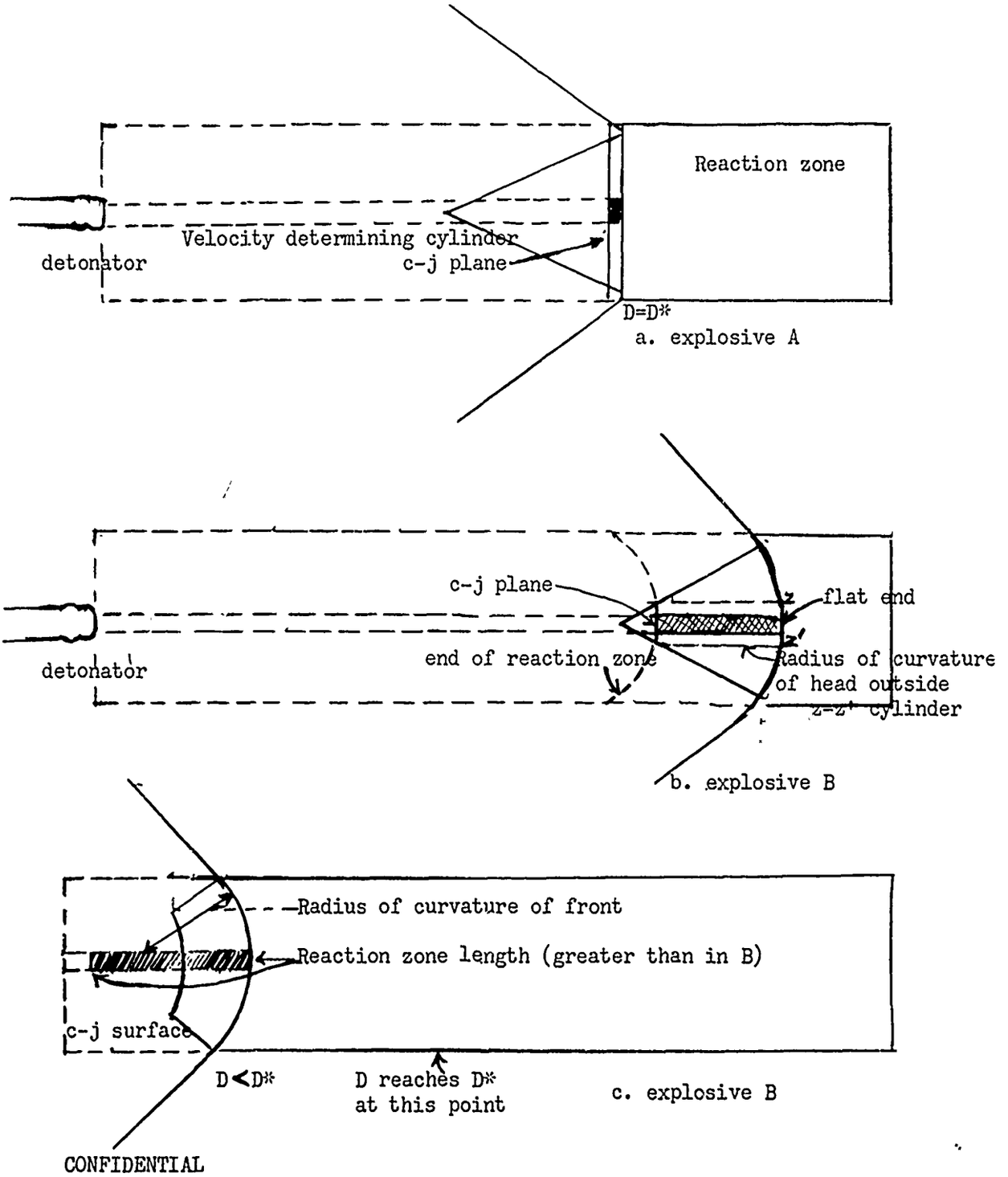

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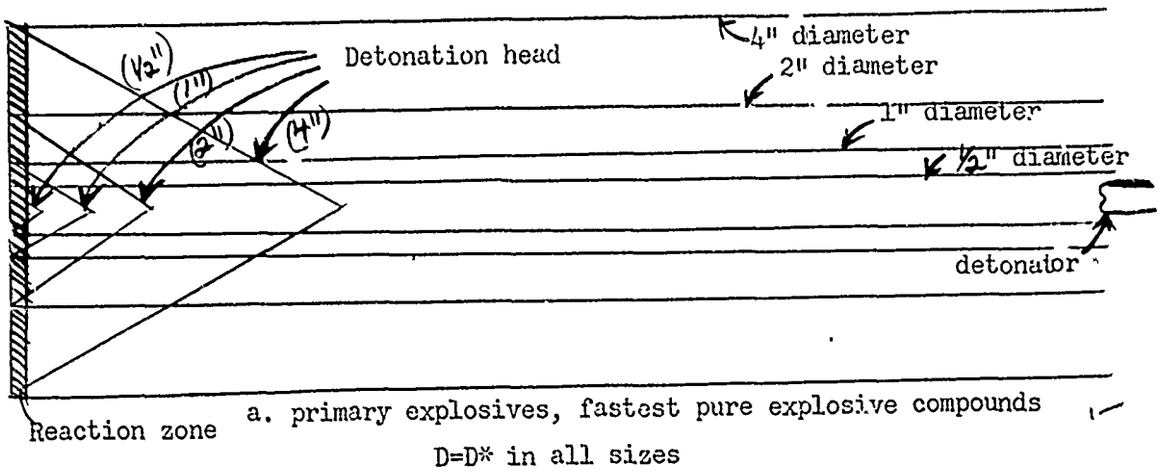
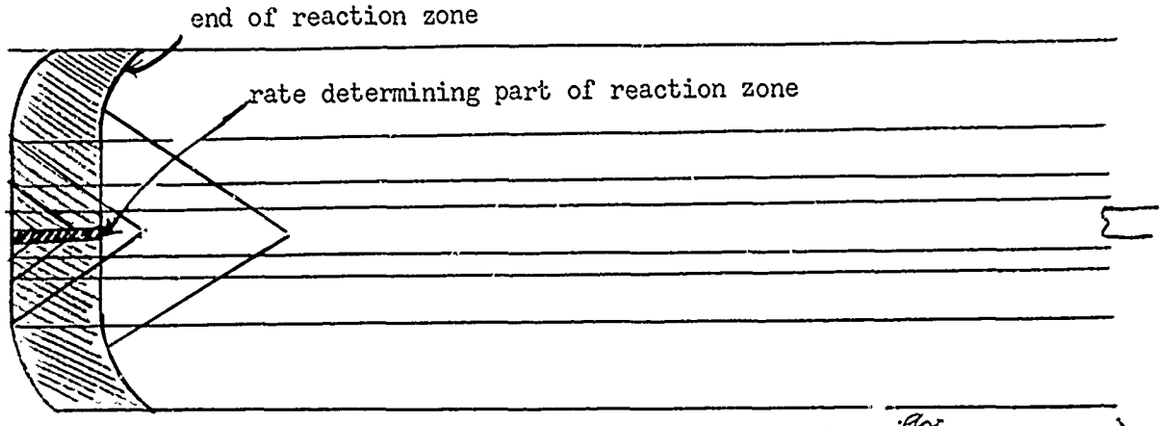
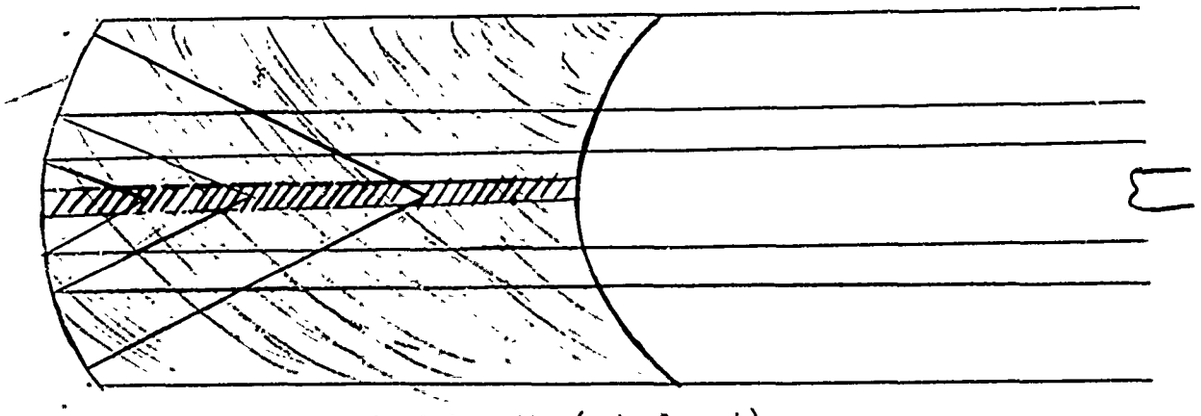
Fig. 6 Relation Between Reaction Zone and Detonation Head



a. primary explosives, fastest pure explosive compounds
D=D* in all sizes



b. Slower pure coarse explosive compounds (e.g. average dynamite)
D<D* for dia ≤ 1 1/2" D=D* for Dia ≥ 1 1/2"



c Slow coarse grained dynamite (not slowest)
D <D* for dia ≤ 6"

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Since the height of the detonation head should be approximately the diameter of the charge, the velocity will increase with the diameter in non-ideal explosives until at some particular diameter, it will become ideal after propogation has proceeded beyond three charge diameters. However, even in this case, the velocity will climb from somewhat less than D* at the point of initiation to D* at exactly the point that the complete detonation head is developed. These geometrical considerations allow one to compute the total reaction time from experimental velocity data. Since it is also possible to measure reaction rates directly in some cases, by other means, it is possible to evaluate the model in considerable detail experimentally. This geometrical method, in fact, allows the determination of reaction rate (or total reaction time) by three independant methods as follows:

(1) The variation of D with charge length. For a non-ideal detonation, or for one which just becomes ideal with the development of the complete detonation cone, one should obtain a velocity vs. distance curve of the type shown in Fig. 7, curve (1). Curves (2) and (3) are velocity vs. charge length curves for ideal detonation with reaction zones of length half the complete detonation head cone height, and small compared with this height, respectively.

(2) The variation of velocity with charge diameter. The velocity in this case is that constant velocity attained after the wave has propogated at least three charge diameters, i.e., where the length/diameter ratio is greater than 3. Typical curves are illustrated in Fig. 8. The reaction zone length and full cone height coincide at the diameters indicated by the arrows. From these points one obtains the total reaction time directly.

(3) With an appropriate reaction rate law, one may compute the total reaction time from a single velocity measurement obtained at a charge length/diameter ratio greater than 3, if the D/D* is less than unity.

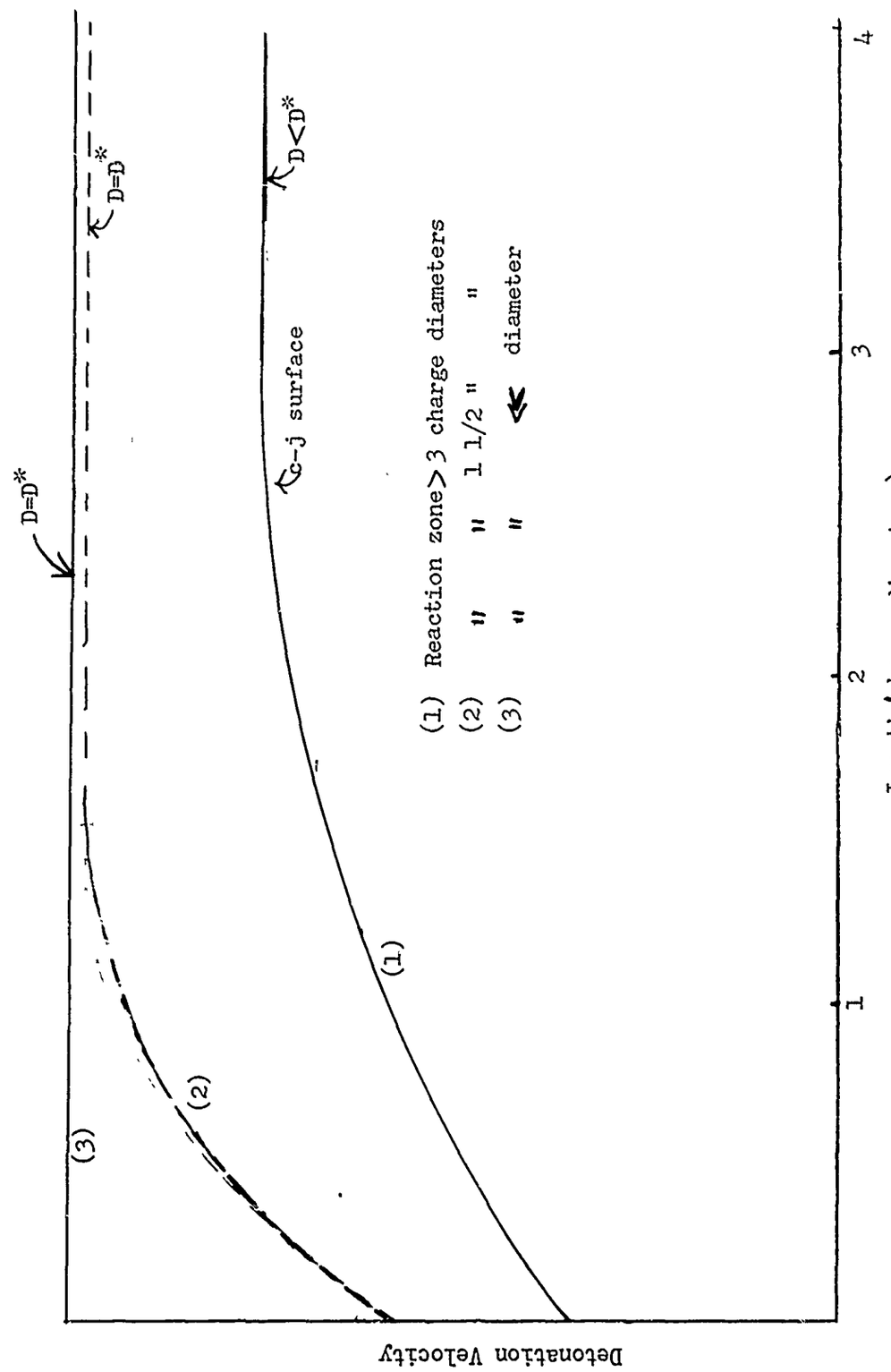

Fig. 7 Characteristic Velocity vs. Charge Length Curves

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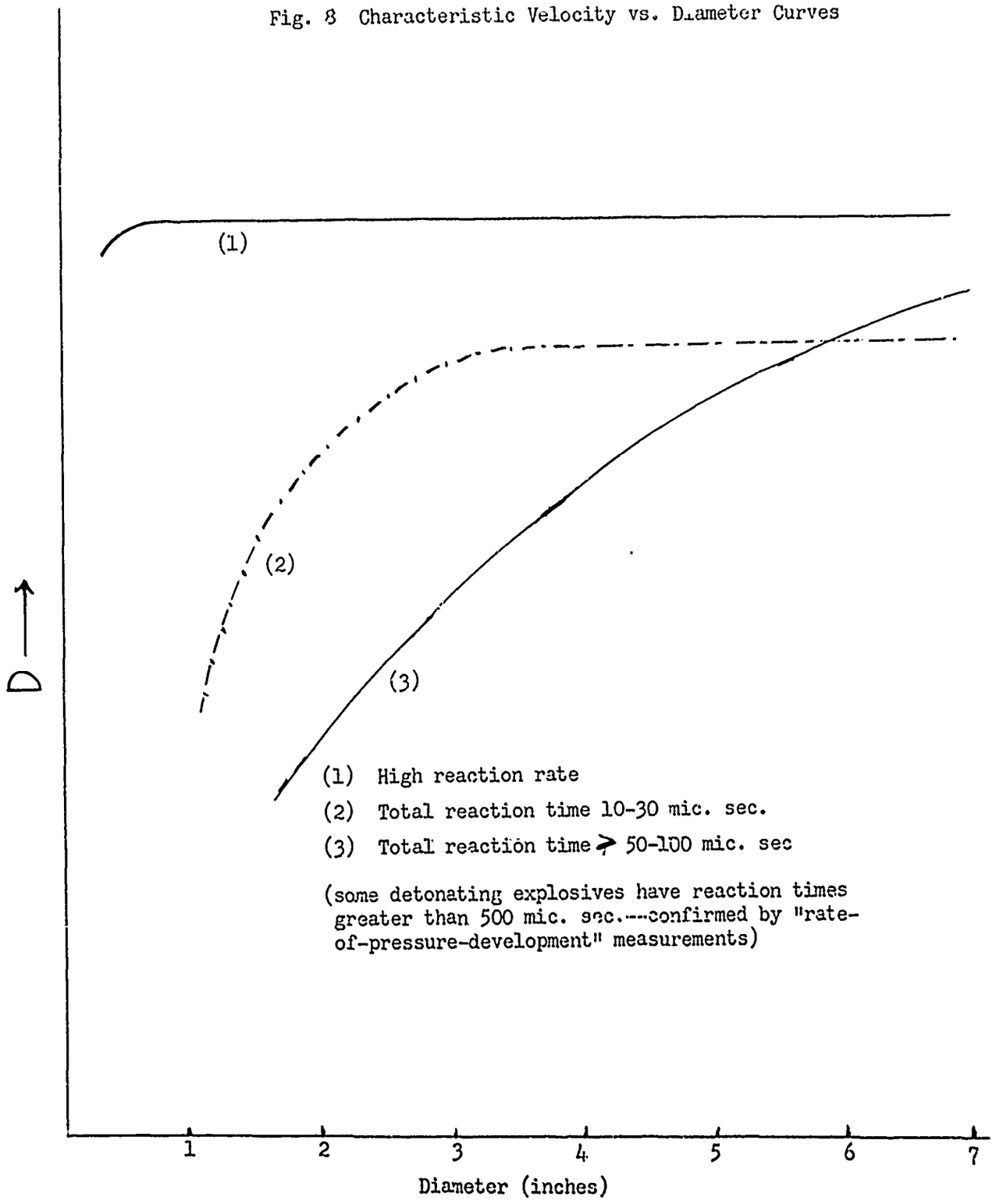
Fig. 8 Characteristic Velocity vs. Diameter Curves



(1) High reaction rate

(2) Total reaction time 10-30 mic. sec.

(3) Total reaction time ≥ 50-100 mic. sec

(some detonating explosives have reaction times greater than 500 mic. sec.---confirmed by "rate-of-pressure-development" measurements)

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Quantitive Reaction Rate Determination

Using the equation of state

$$pv = nRT + \alpha(v)p \tag{3}$$

the ideal detonation velocity D* is given by the equation

$$D^* = \frac{v_1}{v_1 - \alpha^*} \frac{\beta^* + 1}{(\beta^*)^{1/2}} (n^* R T_2^*)^{1/2} \tag{4}$$

where

$$\beta^* = \frac{C_v^* + n^* R}{C_v^*} - \left(\frac{d\alpha}{dv}\right)^* \tag{5}$$

In the $\alpha(v)$ approximation, it has been shown empirically that the same $\alpha(v)$ curve applies apparently to all explosives. This pertains not only to those which produce all gaseous products of detonation, but even to those which have high percentages of "solid residues". This fact, which in itself supports the $\alpha(v)$ approximation, suggests that, except for small variations in v_2/v_1 with the extent of reaction in the detonation head, α and β will depend principally only on the specific volume v_1 and not to any appreciable extent on the completeness of chemical reaction which takes place in the detonation head. The D/D* ratio for non-ideal explosives should therefore, be given approximately by the equation

$$\frac{D}{D^*} \cong \left(\frac{nT_2}{n^* T_2^*}\right)^{1/2} \tag{6}$$

For a chemically homogeneous explosive in which n and Q do not vary appreciably with the pressure, one may express Q and $\bar{C}_v$ for D/D* ratios less than unity by the relations

$$Q^* \, n/n^* \cong Q \quad \text{and} \quad \bar{C}v^* \, n/n \cong \bar{C}v$$

The latter relation assumes, in accordance with the Eyring theory,[9] that the reaction is a surface one and that the heat wave does not penetrate the solid explosive ahead of the reaction flame. Substituting these relations together with the equations

$$T_2 = \frac{Q + \bar{C}_v T_1}{\bar{C}_v - nR/2\beta} \qquad \text{and} \qquad T_2^* = \frac{Q^* + C_v^* T_1}{\bar{C}_v^* - n^* R/2\beta}$$

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into equation (6) one obtains the very simple approximate equation

$$\frac{D}{D^*} = \left(\frac{n}{n^*}\right)^{1/2} = N^{1/2} \qquad (7)$$

where N is the fraction of the explosive which has reacted in the detonation head in the thin cylinder along the central axis of the charge.

Now, the total time τ' during which chemical reaction can contribute to the detonation head characteristics and intensity cannot exceed the value given by the equation

$$\tau' = h/(D-\bar{W})$$

where h is the height of the detonation head cone (truncated or complete, depending on the position of the wave front) and $\bar{W}$ is the average particle velocity in the detonation head, which would be W_{c-j} for the ideal "flat topped" head, represented by curve (1) fig. 1. The total reaction time τ will be either longer (for $D<D^*$) or less (for $D=D^*$) than τ' given by equation (7) except in the case where the total reaction zone and back of the detonation head coincide. In the latter case, τ and τ' would be the same.

Rate Law in Detonation Head

The reaction mechanism proposed by Eyring, et. al.[9] is a surface burning one in which it is assumed that the reaction proceeds into the grain at a rate determined by the temperature and the pressure of the gases in contact with the surface. The surface temperature T is, in other words, assumed to be the same as that of the gases to which the grains are exposed. It is also assumed that the interior of the grain is at the original temperature T_1 while the grain is being consumed. That is, the heat wave front and reaction flame are assumed to coincide in the burning of the grain in the detonation head. Since in general, the rate of consumption of the grain (in a detonation reaction slow enough to be non-ideal) is slow compared with the translational velocity of the products of detonation and the rate of energy transfer in these gases, the establishment of equilibrium, both chemical and thermal, will be assumed to be complete in

the gas phase at all times during the explosive reaction, at least in as far as the local regions of the particle are concerned. There may, however, exist a temperature and density gradient throughout the reaction zone as indicated previously.

One requires a knowledge of T(x) in the reaction zone for the various assumed W(x) relations in order to compute accurately the rate of reaction from total or effective reaction times. Suppose for example, one were dealing with a "flat topped" detonation head in a pure explosive compound in which the reaction products were relatively independant of pressure, T would then be practically constant throughout the reaction zone and equal to T_2 (the temperature at c-j plane). If, then, the rate in the detonation head (or the activation energy $\Delta F^{\ddagger}$) were independant of pressure (which has been found in the cases so far studied) but dependant only on T, the rate of reaction in detonation could be determined from the effective reaction time τ' in the detonation head and the observed D/D^* ratio. On the other hand, even in a reaction zone of variable W(x), the temperature variation should not be large.[9] Moreover, the temperature coefficient of the reaction rate would be relatively small, at detonation temperatures. For example, in contrast with the generalization frequently made that chemical reaction rates (at room temperature) double with each 10° rise in temperature, one requires a 300° C increase in temperature at around 4000°K to double the rate of reaction for a heat of activation $\Delta H^{\ddagger}$ of 70 K. cal/mol, and a still greater increase in temperature to double the rate for lower heats of activation (at $\Delta H^{\ddagger}$ = 50 K. cal/mol, the temperature increase would need to be about 500° in order to double the rate at 4000° K).

The greatest possible variation in T (x) between the wave front and the C-J plane, i.e., between x_a' and x_{cj}, would probably be that given by the relation

$$\bar{T}_2 - T(x) = \frac{Q^+ \pm \frac{1}{2}W_{cj}^2}{\bar{C}_v^*} - \frac{Q(x) \pm \frac{1}{2}W(x)^2 \cdot N(x)}{\bar{C}_v} \qquad (9)$$

where $Q(x) = N(x)Q^*$ and $\bar{C}v = N(x)\,\bar{C}v^*$, with $N(x)$ the fraction of explosive reacted at the position x along the charge axis. This gives

$$T_2 - T(x) = \frac{+W_{cj}^2}{2\bar{C}_v^*}\left(1 - \frac{W(x)^2}{W_{cj}^2}\right) \qquad (10)$$

the coefficient $1/2\ Wcj^2/\bar{C}v^*$ amounts to from 500° to 1000° for densities from 0.8 to 1.6 in an average explosive. The average difference $T_x - T(x)$ in the reaction zone should, therefore, be small enough, particularly if one were to study reaction rates at low charge densities, that the use of a constant $T(x) = T_2$ would lead to reaction rates in error by less than a factor of two, since heats of activation of most explosives will be 50 K cal./mol or less. One should thus make no appreciable error in computing reactions rates from total reaction times (τ'), obtained by the above methods, by assuming that the temperature of reaction in the part of the reaction zone coming within the detonation head is constant and equal to T_2 - the value at the C-J plane.

The isothermal decomposition of many explosives at temperatures below their so-called "explosive temperature", i.e., in the range of 100-200°C, are first order, according to the equation

$$\frac{dN}{dt} = K'(1-N) = \frac{kT}{h} e^{\frac{-\Delta F^{\neq}}{RT}} (1-N) \qquad (11)$$

In detonation these reactions are expected to be first order with respect to the surface concentrations only since, presumably, the temperature T(x) applies only at the surface. Eyring [9] has shown that this leads to an apparent or pseudo two-thirds order law. For a surface reaction of this type, one may write

$$\frac{dn'}{dt} = k' \frac{4\pi r^2}{s} = \frac{4\pi r^2}{v} \frac{dr}{dt} \qquad (12)$$

for a particulate explosive of uniform particle size. Here n' is the number of molecules reacting, r the grain radius, s the effective molecular cross-sectional area and v the volume per molecule. Since

$$N = 1 - \left(\frac{r}{r_1}\right)^3$$

where r_1 is the original grain radius, one obtains

$$\frac{dN}{dt} = \frac{3k'v}{r_1 s}(1-N)^{2/3} = \frac{3}{\tau}(1-N)^{2/3} \qquad (13)$$

where $\tau = \frac{r_1 s}{k'v}$ is the total reaction time. The integrated form of equation (13) is

$$N(t) = \left(1 - \frac{t}{\tau}\right)^3$$

where t is the time.

In summary, since N(t) may also be determined from the theory of the detonation head, by means of equation (7), it is feasible to evaluate the concepts outlined here by a number of independant means as follows:

(1) By a comparison of computed and experimental velocity vs. diameter curves.

(2) Comparisons with τ''s computed from the D(dia)/D* ratio with those of low temperature thermal decomposition data.

(3) Direct "rate-of pressure-development" measurements in explosive in which D/D^* is considerably less than unity.

(4) Comparisons between reaction times computed by this method and those from the curved front method of Eyring, et. al., using observed data for the curvature of the front.

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